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Single-donor impurities and core excitons in many-valley semiconductors

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We discuss our previous results in the perspective of recent developments. We argue that intervalley kinetic and overlap terms are artifacts of a different incorrect formalism, and we thus maintain our prediction of deep interstitial and substitutional single donors and core excitons in Si. We outline an experiment in which the intervalley effect, the core-hole-electron interaction, and the shallow-deep instability may all be directly observable in Si.

I. INTRODUCTION

In this paper (Sec. II) we discuss in more detail the results of a previous paper.[1] We then proceed (Secs. III and IV) to discuss the objections which have been recently raised by some authors.[2,3] They claim that a basic contribution, the so-called intervalley kinetic-energy term T_{inter}, has been neglected in the apporach which we propose[I8,I9,1] (I denoting a reference to an equation or reference in our preceding paper[1]). We show that such a term should not exist in a correct formulation and we thus maintain our prediction of deep interstitial and substitutional donors and core excitons for the screened point-charge potential $V_d(r)$ of Eq. (I11) and the intervalley constructive interference in Si.

It appears by now, proven experimentally, that core excitons are deep in many-valley semiconductors.[I6,I7,4] It may be possible to obtain definite experimental evidence that the responsible mechanism is the one which we outline. We propose (Sec. V) one such possible experiment, namely the optical study of deep core excitons in Si under uniaxial stress in the [100] direction.

II. COMMENTS TO THE RESULTS OF THE PRECEDING PAPER

The preceding paper[1] may leave the following questions unanswered. The basic point is that all results fall in two regimes: one where the effects are small and the results are close to the effective-mass theory (EMT), and a second, where the binding is extremely different. In the first regime, it may not be apparent what the importance is of the small differences from EMT. In the second, it may not be clear to which extent the lowest-band approximation has broken down for all the cases given and also for core excitons in Si, and then how many bands are needed on the deep cases and what are the extensions to multiple bands.[5]

In the cases in which the differences from the EMT are small we conclude that the approximations which we made are consistent and justified. In particular, the single-band approximation is valid, and Eqs. (I8) and (I15) give the same results. This regime occurs when either the impurity potential $V(r)$ diverges slower than r^{-1} around the origin, or the intervalley interference is not constructive around the origin. In this regime the significance of this new method is to provide a *simple* and accurate generalization to the EMT, which consistently includes the many-valley effect. Therefore, the differences with respect to the EMT must be regarded as physically meaningful. However, we have not yet performed a systematic study of those differences or a detailed comparison with the experimental data. We have shown that, in order to do so, it is also necessary to introduce reliable first-principle impurity pseudopotentials $V(r)$, *other than* those of Eqs. (I10) and (I11). We discuss in further detail this last point in both Secs. III and IV.

When the binding energies differ for orders of magnitude from the EMT results, the single-band approximation has broken down. This is shown by the quite different results of Eqs. (I8) and (I15). The calculated binding energies are meaningless, but the prediction of a deep state is correct. In fact, if the state were shallow, its wave function would have automatically been confined to the lowest conduction band (CB) to begin with, the single-band approximation would have been justified, and there would have not been any instability in Eq. (I8) in the first place. We have shown that the deep state regime occurs whenever the potential $V(r)$ diverges as r^{-1} around the origin and the intervalley interference is constructive therein, regardless of whether that origin is interstitial or substitutional.

If one attempts to calculate in detail the binding energy of an intermediate or a deep state by means of an expansion on energy bands, he must consider an energy range approximately as large as twice the binding energy of the deep state (Sec. III of Ref. 1). Equations which include generalizations to multiple bands have been introduced.[6] However, the real problem comes at the point when one has to perform some actual calculations. So far, it appears that nobody has attempted any detailed calculation starting from the EMT point of view and including multiple bands, with perhaps the exception of Mieher *et al.*, in Refs. I12 and I13 and related papers. We discuss in more detail the multiple-band expansion in Sec. III.

III. THE INTERVALLEY KINETIC-ENERGY TERM

Some authors[2,3] have recently attributed the differences between their results and ours to an off-diagonal term allegedly produced by the unperturbed Hamiltonian H_0, the so-called intervalley kinetic-energy term T_{inter}. The absence of such a term was previously deduced and pointed out.[I8,I9,I18,1] Further discussion still appears to be needed.

The Hamiltonian for the impurity problem is

$$H = T + V_{\text{cryst}}(\vec{r}) + V(r) , \tag{1}$$

where

$$T = -\frac{\hbar^2 \nabla^2}{2m_e} , \tag{2}$$

is the true kinetic-energy term, which contains the true electron mass m_e, $V_{\text{cryst}}(\vec{r})$ is the perfect-crystal periodic potential, and $V(r)$ is the potential-energy difference introduced by the defect. Two basic approaches are possible, depending on whether one is attempting to describe a shallow or a deep state. In the first case one considers

$$H_0 = T + V_{\text{cryst}}(\vec{r}) , \tag{3}$$

as the unperturbed Hamiltonian, and $V(r)$ as the (small) perturbation. One then expands the impurity wave function $\psi(\vec{r})$ onto the eigenstates of H_0. By doing so, the (complicated) operator H_0 becomes diagonal and simply given by its (real number) eigenvalues

$$H_0 \cong E_c(\vec{k}) , \tag{4}$$

which are (assumed to be) known. Similarly, in the second case of a deep level, one considers

$$\mathscr{H}_0 = T + V(r) , \tag{5}$$

as the unperturbed Hamiltonian, and $V_{\text{cryst}}(\vec{r})$ as the (small) perturbation. Likewise, one then expands $\psi(\vec{r})$ onto the eigenstates of $\mathscr{H}_0$, etc.

The EMT, as well as any other method which attempts to describe shallow states to begin with, must use the first approach, and eventually make the further assumption that the expansion is localized around the conduction-band (CB) minima. In that case, one can retain the quadratic term only in the expansion of Eq. (4):

$$E_c(\vec{k}_\mu + \vec{\eta}) \simeq \frac{\hbar^2 \eta^2}{2m^*} . \tag{6}$$

However, it should remain understood that H_0 can be identified with the expression (6) only on the basis of its own eigenstates, on which it is diagonal. Therefore, it is not possible to have off-diagonal elements of the expression (6), the so-called T_{inter}, unless one has chosen an incorrect set for the eigenstates of H_0. In that case Eqs. (4) and (6) cannot be assumed, and $T + V_{\text{cryst}}(\vec{r})$ becomes in fact an intractable operator, which has nothing to do with the Hamiltonian of a free particle of mass m^*.

We have correctly assumed from the beginning (Ref. I8) that $\Phi(\vec{\eta},\vec{r})$ as given in Eq. (I2) is an orthonormal set of eigenstates of H_0, correct and complete within the single-band approximation. Therefore, whenever such approximation is justified, Eq. (I8) stands correct without any T_{inter} or "intervalley overlap term" O_{inter}. Consequently, all the results which we derive from Eq. (I8) are also correct, including the prediction of deep levels for the screened point-charge potential $V_d(r)$ of Eq. (I11) and the A_1 symmetry, for both interstitial and substitutional donors and core excitons in Si.

Let us now determine how the basis (I2) should be correctly enlarged in order to describe states beyond the single-band approximation. One must clearly assume (from an "extended zonelike" point of view) that, whenever η exceeds η_c, as given by Eq. (I13), the Bloch functions $\psi_c(\vec{k}_\mu+\vec{\eta},\vec{r})$ automatically refer to the second (or eventually the higher portion of the lowest) conduction band (see Fig. I3). With this (obvious) understanding, the set (I2) remains clearly an orthonormal basis of eigenstates for H_0, correct and complete within the second- (or higher) band approximation. Equation (4) remains valid, no T_{inter} or O_{inter} can ever appear anywhere. Notice that Eq. (I8) should remain valid far beyond the single-band expansion, as far as the basis is concerned. The expressions which can no longer be justified beyond the single-band approximation are instead the expansion (6) and the plane-wave-like approximation (I5) in the calculation of the matrix elements of $V(r)$.

The authors of Refs. I10, 2, and 3 retain the expansion (6) and the approximation (I5). In addition, they perform an approximation on the matrix elements of $V(r)$, which is very questionable except maybe for very small η values (see Refs. I9 and 7). On the other hand, as far as H_0 is concerned, they let $c(\eta)$ extend beyond η_c, and then perform a different choice of the basis set. That consists in taking always the $\psi_c(\vec{K}_\mu+\vec{\eta},\vec{r})$ which are associated to the lowest CB, no matter what η is. The result is that the set (I2) is no longer orthonormal [see Eq. (4) in Ref. 2], and it is certainly not a correct set of eigenstates of H_0 for the considered range of η values. Consequently, Eqs. (4) and (6) could no longer be assumed. Equation (5) of Ref. 2 indeed reads

$$\langle \Phi(\vec{\eta},\vec{r})\,|\,H_0\,|\,\Phi(\vec{\eta}',\vec{r})\rangle=\frac{\hbar^2\eta^2}{2m^*}\delta(\vec{\eta}-\vec{\eta}')+\sum_{\mu,\nu}{}'\alpha_\mu\alpha_\nu E_c(\vec{k}_\nu+\vec{\eta}')\delta(\vec{k}_\mu+\vec{\eta}-\vec{k}_\nu-\vec{\eta}')\ . \tag{7}$$

The first term in the right-hand side is the only one which should remain, if the definition of $\Phi(\vec{\eta},\vec{r})$ was understood appropriately for $\eta>\eta_c$. The second term is the one that originates T_{inter}, and arises because $\Phi(\vec{\eta},\vec{r})$ is forced into the lowest CB also for η values larger than η_c. In other words, Eq. (7) implies an expansion which involves (many) more states that those which are complete for the lowest CB. However, the additional states are always taken from the lowest CB. Each state of the lowest CB is thus multiply counted with different matrix elements. On the other hand, any other state of any higher band is disregarded. Such a choice of the basis set is inconsistent. Either the expansion requires only the states of the lowest CB ($\eta\le\eta_c$), in which case those states must be counted once and no other state is considered; or the expansion requires more states than just those of the lowest CB ($\eta>\eta_c$), in which case the states of the higher bands must be considered, rather than counting more times again the states of the lowest CB with different matrix elements.

Furthermore, Eq. (7) is inconsistent because the expansion (6) is used in the first (diagonal) term, but not in the second (intervalley) term. In principle, one cannot let $E_c(\vec{k}_\nu+\vec{\eta}')$ in Eq. (7) to raise quadratically beyond $\eta>\eta_c$, otherwise he is practically associating eigenvalues of higher bands to eigenfunctions of the lowest CB. In such case, the second term of Eq. (7) would also become completely meaningless, since $E_c(\vec{k}_\mu+\vec{\eta})$ could be different from $E_c(\vec{k}_\nu+\vec{\eta}')$ [see Eqs. (8a) and (8b)]. Consequently [see, for example, Eqs. (22) and (23)] and the corresponding discussion in Ref. 3, $E_c(\vec{k}_\nu+\vec{\eta}')$ is (partially) restricted to the lowest CB, by means of a truncation. Suppose, for example, $\vec{\eta}=\frac{1}{4}(\vec{k}_1-\vec{k}_2)$ and $\vec{\eta}'=\frac{3}{4}(\vec{k}_2-\vec{k}_1)$. The choices are:

$$E_c(\vec{k}_1+\vec{\eta}')=E_c(\vec{k}_1+\tfrac{3}{4}\vec{k}_2-\tfrac{3}{4}\vec{k}_1)=\frac{9}{16}\frac{\hbar^2\,|\,\vec{k}_2-k_1\,|^2}{2m^*}\ , \tag{8a}$$

or

$$E_c(\vec{k}_1+\vec{\eta}')=E_c(\vec{k}_2+\tfrac{1}{4}\vec{k}_1-\tfrac{1}{4}\vec{k}_2)=E_c(\vec{k}_2+\vec{\eta})=\frac{1}{16}\frac{\hbar^2\,|\,\vec{k}_1-\vec{k}_2\,|^2}{2m^*}\ . \tag{8b}$$

The second choice (8b) must result for the second term of Eq. (7), which should be achieved by means of the truncation. However, no truncation is performed for the first term of Eq. (7), and the first choice (8a) is kept on that. From the numerical point of view, such inconsistency amounts to the following. If one assumes the expansion (6) with no truncation, that produces a sizeable intravalley (diagonal) kinetic-energy term T_{intra}, but then there cannot be any T_{inter} at all. If one includes T_{inter}, the expansion (6) must be truncated for T_{intra} as well, which amounts to a severe reduction of T_{intra} for a localized state in $\vec{r}$ space. Either way, the numerical result should not differ qualitatively from ours. However, the authors of Refs. I10, 2, and 3 both introduce T_{inter} *and* yet leave total strength to T_{intra}, since they do not limit the indefinite quadratic raise (6) associated to it. That could well be the major reason for a huge overestimate of the kinetic-energy term. On the other hand, no truncation whatsoever on the potential-energy term is performed in Refs. I10, 2, and 3. We must also notice that the truncation for the second term of Eq. (7) is not performed at the zone boundary $\eta_t = \eta_c$ but midway between the different minima in the first Brillouin zone.[3] That corresponds to η_t much larger than η_c, which boosts even more (incorrectly) T_{inter}. The calculations of Refs. I10, 2, and 3 are complex and require further approximations for the calculation of T_{inter}. Therefore, we are not in any position to reproduce and study quantitatively the various (spurious) contributions which we mentioned.

In conclusion, T_{inter} and O_{inter} are artifacts of an incorrect formalism, and do not have any theoretical justification. The effect that they create, namely a strong compensation of the deepening produced by $V_d(r)$, is artificial. In reality, proper inclusion of higher bands can only stabilize the solution within their corresponding energy range. It cannot reduce the binding energy within the range of the lowest CB, when it has in fact been shown that the solution is unstable in such a range. The potential $V_d(r)$ is unstable (regardless of its location) and the binding energy of its ground state is much larger than the energy range of the lowest CB. The only way to correctly obtain shallow ground states is to assume a short-range cutoff to $V_d(r)$ (Refs. I8, I9, and 1). In this respect, notice in Table (I1) that even the shallow levels of $V_d(r)$ are anomalous for the A_1 symmetry, since they appear to be shallower than the corresponding ones of $V_s(r)$, even though $V_d(r)$ is everywhere stronger than $V_s(r)$. The reason is, of course, the presence of the deep levels through the orthogonality conditions. That is ultimately, again, a consequence of the critical behavior of $V_d(r)$ at the origin.

It may be tempting[8] to try to establish some correspondence between the introduction of T_{inter} and O_{inter} and the "filter" of Eqs. (I13)–(I20). They both force, in some sense, the solution within the lowest CB. There is, however, a basic difference. The latter is a rigorous procedure of limiting the expansion of $\psi(\vec{r})$. One then knows that only shallow states can result from that, and all Fourier components of $V(r)\,|\,\Phi(0,\vec{r})\,|^2$ with $\eta > \eta_c$ are eliminated. If one knows *a posteriori*, typically from experimental data, that some levels are shallow, Eq. (I15) or Eq. (I20) can predict them accurately, regardless, to a large extent, of irregularities or uncertainties in the potential $V(r)$. Shallow donors in Si and Ge are in fact correctly reproduced by Eqs. (I15) and (I20), using quite simple and flexible [and yet unstable for Eq. (8)] model potentials $V(r)$ (Refs. 8 and 9). On the other hand, the introduction of T_{inter} and O_{inter} does not provide a justifiable and rigorous restriction to the lowest CB and to shallow levels. The possibility of a shallow-deep instability can always be present. The authors of Refs. I10 and 2 experience that, depending on the location of the defect. The basic reason is that the potential-energy term can always be large (and overestimated) for a localized state in $\vec{r}$ space, if the expansion of $\psi(\vec{r})$ is not limited to the lowest CB. Indeed, since the $\Phi(\vec{\eta},\vec{r})$'s are approximated as in Eq. (I5) for the potential-energy term, they cannot be orthogonal when η extends beyond η_c. That produces an overestimate as it is easily seen in the limit of a constant potential.[1]

IV. THE POTENTIAL-ENERGY TERMS

From the discussion of Sec. III it is clear that the impurity potential $V(r)$ may always have off-diagonal elements V_{inter}, since $\Phi(\vec{\eta},\vec{r})$ has nothing to do with its own eigenstates. For instance, Eqs. (I14)–(I17) describe an impurity wave function $\psi(\vec{r})$ rigorously localized within the lowest CB, without any "spilling" of the tails of $c(\vec{\eta})H(\eta-\eta_c)$ between different neighboring valleys. And yet if we consider, say,

$$V(r) = -v_0\delta(\vec{r}) \,, \tag{9}$$

the second term of Eq. (I15) yields

$$-v_0\Delta_{\eta_c}(\vec{r})\,|\,\Phi(0)\,|^2 G(0) \,, \tag{10}$$

which shows that $V(r)$ produces intervalley coupling between different neighboring valleys. Now, if we make a proper extension to multiple bands, $V(r)$ can couple both different valleys and different bands, whereas H_0 must always remain rigorously diagonal with respect to both. Therefore, we do not agree with the multiple-band extension of Ref. 6, since those equations again contain intervalley kinetic-energy terms.

In Ref. 2 Altarelli disregards the criticism which we made (Ref. I9) to their approximation (Refs. I10 and 7) on the matrix elements of $V_d(r)$. He warns "that a function with *exponential* localization in $\vec{r}$ space, $F(\vec{r})\sim e^{-\gamma r}$, corresponds to a function with *algebraic* localization in $\vec{k}$ space, $c(\vec{\eta})\sim(\gamma^2+\eta^2)^{-2}$." That is apparently too weak of a localization with respect to the quadratic raise of $E_c(\vec{\eta})$, and allows for the large effects of T_{inter}. However, their approximation on the matrix elements of $V_d(r)$ [see for instance Eq. (4) in Ref. 7] essentially consists of multiplying by

$$\frac{|\vec{k}_\mu+\vec{\eta}-\vec{k}_\nu-\vec{\eta}'|^2}{|\vec{k}_\mu+\vec{\eta}-\vec{k}_\nu-\vec{\eta}'|^2},$$

and then set $\underline{\eta}=\vec{\eta}'=0$ in the numerator, invoking the localization of $c(\vec{\eta})$. This also produces a quadratically increasing error on V_{inter}. Our results in Table I1 show a dramatic reduction in the potential-energy term due to such an approximation for the substitutional case, and in fact a resulting shallow state rather than a deep one. Unfortunately, all the results of Table I1 appear to be quite different from those of Table I in Ref. 2, regardless of whether T_{inter} and O_{inter} are included or not, and even though all the parameters are taken to be essentially the same.

The screened point-charge potential $V_d(r)$ is critical, since it can effectively couple at any location, different valleys and different bands. Therefore, $V_d(r)$ is unstable and it has the capability of producing deep levels. This is confirmed by the experimental evidence concerning interstitial hydrogen and muonium in Si (Ref. I4). We have no reason to believe that the same effect should not take place for a substitutional defect as well.[I8,I9,1] Hence, we must conclude that $V_d(r)$ by itself is not appropriate to describe any of the well-known shallow donors, including the isocoric substitutional donors such as P in Si. A clear justification for that is given in the concluding remarks of Refs. (I8) and (I9). The same argument has been independently provided in Ref. 6. On the other hand, other authors[I10,7] claim that $V_d(r)$ is, in fact, appropriate for the isocoric substitutional donors. At the same time, they also claim[2] that $V_d(r)$ "appears to be an upper limit of short-range strength for the group-V donors in Si." These two statements contradict each other in view of the experimental evidence[I1–I3] that the ground state of As in Si has a larger binding energy than P. In Ref. 3 the opposite is then assumed, that is, $V_d(r)$ is attributed to As, rather than to P. It is also not very clear why a potential stronger than $V_d(r)$ around the origin should be attributed to N, as implied in Ref. 2, to take care of the fact that N appears to be a deep substitutional donor.[I11]

In conclusion, there is substantial disagreement about the attributions to specific impurities of particular pseudopotentials $V(r)$, and their relative parameters. In this respect we agree with the conclusion of Ref. 6 that the task of meaningfully performing those attributions will be very sensitive. This should perhaps suggest that one should check the approximations of his equations more carefully before proceeding with his choices of impurity pseudopotentials, since he may easily reach superb agreement with most experimental data and still have an incorrect theory.

V. A POSSIBLE EXPERIMENT ON CORE EXITONS

Core excitons in semiconductors are at present not really understood. Several models and theories have been proposed, invoking electronic polaron effects, nonlocality of the electron-hole interaction (local-field effects), time dependence in the dielectric screening, hole lifetime effects, interaction with phonons, and other mechanisms.[10] All these models and theories conclude that there cannot be any large binding energy far beyond the EMT range. However, the experimental evidence seems to indicate definitely the opposite.[I6,I7,4] Other models introduce large binding energies as an "*ad hoc* assumption", or invoke surface effects in the interpretation of the experimental data.[10] It appears that the mechanism which we propose is the simplest and yet the only one which predicts large binding energies quite consistently and naturally.[10] The basic assumptions are the screened point-charge potential $V_d(r)$ to represent the electron-core-hole interaction and the intervalley constructive interference. Altarelli still concludes[2] that "the present understanding is that intervalley effects cannot be invoked to predict deep core exciton levels in Si". That is not our present understanding. In any case, the reality may or may not correspond to these (quite simplified) models. The electron-core-hole interaction is a complex manybody problem, not quite understood even in free atoms. The intervalley effect is a model picture a long way from first principles. Therefore, only the experimental evidence may indicate whether or not there is a real physical meaning to be given to the formalisms which we make. We thus propose the experimental study of core excitons in Si under uniaxial stress in the [100] direction. Such uniaxial stress produces a removal of the degeneracy of the six equivalent minima of the conduction band.[I1,I2,11] They split into a pair and a quadruplet, and the latter moves towards higher energies. The splitting is about 9 meV/kbar,[11] and compressions as high as 15∼20 kbar are attainable. On the other hand, the secondary minima at L are about 1 eV higher in energy and they should never enter the picture (by producing some appreciable mixing). Therefore, it is possible, by means of a (high) uniaxial stress, to practically reduce the number of equivalent minima in Si from six to two. According to our calculations such a reduction should rapidly push the deep core excitons back into the shallow regime, and a strong nonlinear decrease in the binding energy of those levels should be observed with increasing stress. In other words, such an experiment may constitute the actual observation of the deep-shallow instability produced by the (critical) potential $V_d(r)$ and the intervalley interference.

Optical experiments on core excitons in $\mathrm{GaAs}_{1-x}\mathrm{P}_x$ under uniaxial stress have already been performed recently.[4,12] That has further contributed to a consistent picture and analysis of those levels. The deep character is confirmed, as well as the identification of the components of the levels in terms of the minima of the conduction bands. There is however no evidence of any steep decrease in the core-exciton binding energies, such as that which we predict in Si. On the other hand, we do not know whether or not there should be any, since we have not performed any detailed calculations on those materials. The theory which is provided in Refs. (I7), 4, and 12 appears to be similar but not equivalent to our model. The basic parameters are fitted from the experimental data, and it is not clear whether or not the deep character of the levels comes as a direct consequence of the intervalley interference. We must also point out that the situation in those materials is much less favorable than in Si from our perspective. In both GaAs and GaP the minima at X and L are not much separated (about 300 meV or less). Therefore, there is substantial mixing among those inequivalent minima already at zero stress. In general, the stress is not likely to remove such a mixing, even though it may considerably split (some of) the equivalent minima. The experiment in Si appears to be much more favorable in that respect, since the (inequivalent) minima at Δ and L are too separated to significantly interfere, either with or without stress. Therefore, stress can reveal the instability associated to the degeneracy of the minima at Δ alone. Such an experiment in Si, even though quite delicate, also appears to be feasible up to the necessary intensity and stress levels, in view of the present techniques.[13]

It is also possible to conceive experiments in which the deep-shallow instability of interstitial single donors may be directly observable. One possibility is the measurement of the muon spin rotation[I4] in Si under high uniaxial stress in the [100] direction. At the moment we have no information on whether or not such an experiment may be practically feasible. The other possibility is to look for the donor levels of interstitial hydrogen. These levels have never been revealed by any experiment or technique, and for that reason they are thought to be deep. However, a high uniaxial compression in the [100] direction should rapidly push them back into the shallow regime (we are, of course, assuming that even though the equivalent minima are significantly split, the corresponding wave functions are not dramatically changed). The hydrogen levels should then become accessible to the very refined infrared spectroscopy techniques.[I1,I2,11] If either one of these experiments can be performed, as well as the one on core excitons mentioned above, one may be able to draw a definite conclusion about the so-called site dependence of the shallow-deep instability.

In conclusion, if the experimental result will be the one which we predict, one should hold it as a strong evidence for the presence of intervalley effects and specifically for the mechanism of intervalley interference in the formation of deep core excitons. One should also gain more confidence that $V_d(r)$ can be a good representation for the core-hole-electron interaction, which is a basic piece of information for the whole present theory and understanding of core excitations. We are at the moment perhaps mostly interested in the first point. If $|\Phi(0,\vec{r})|^2$ proves to have a direct physical meaning as the factor which renormalizes the potential at short distances due to the intervalley scattering, that is a very simple tool to account for the intervalley effects in a large number of problems in semiconductors. For instance: ionized impurity scattering and mobility of electrons; binding energies of single donors as a function of the impurity concentration up to the insulator-metal transition; donor-bound multiexciton complexes;[8,9] field ionization of impurity levels[14,15] and fractional charge impurities.[16]

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